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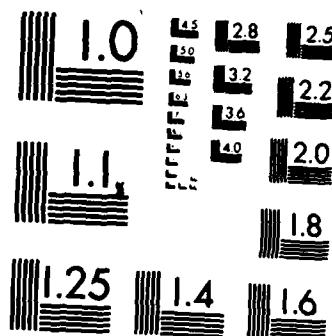
POLYPHOSPHORUS COMPOUNDS CONTAINING PHOSPHORUS-NITROGEN 1/1  
BONDS(U) GEORGIA UNIV ATHENS DEPT OF CHEMISTRY  
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FINAL REPORT

to the

Air Force Office of Scientific Research  
U. S. Air Force  
Bolling Air Force Base, D. C. 20332

on

POLYPHOSPHORUS COMPOUNDS CONTAINING PHOSPHORUS-NITROGEN BONDS

Period Covered:

January 1, 1981, to December 31, 1983

Grant Covered

AFOSR-81-0051

by

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Athens

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER <b>AFOSR-TR- 84-0091</b>	2. GOVT ACCESSION NO. <i>414137722</i>	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) <b>Polyphosphorus Compounds Containing Phosphorus-Nitrogen Bonds</b>	5. TYPE OF REPORT & PERIOD COVERED Final Technical Report: January 1, 1981, to Dec 31, 1983	
7. AUTHOR(s) <b>R. B. King</b>	6. PERFORMING ORG. REPORT NUMBER	
9. PERFORMING ORGANIZATION NAME AND ADDRESS <b>Department of Chemistry University of Georgia Athens, Georgia 30602</b>	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS <i>61102 F 2303 /82</i>	
11. CONTROLLING OFFICE NAME AND ADDRESS <b>Air Force Office of Scientific Research/NC Bolling Air Force Base, D.C. 20332</b>	12. REPORT DATE <i>January, 1984</i>	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	13. NUMBER OF PAGES <i>14</i>	
16. DISTRIBUTION STATEMENT (of this Report)	15. SECURITY CLASS. (of this report) <b>Unclassified</b>	
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
<b>Polyphosphorus Compounds Aminophosphines Cyclopolyphosphines Organophosphorus Derivatives</b>		<b>Phosphorus-Nitrogen Bonds Phosphorus-Hydrogen Bonds Metal Carbonyl Complexes</b>
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
<p><i>The original scientific objective of this basic research program was the understanding of the synthesis and chemical reactivity of organic compounds consisting of a carbon backbone containing several bis(dialkylamino)phosphino substituents, (R<sub>2</sub>N)<sub>2</sub>P. This class of organophosphorus compounds, which has received very little attention, is of potential importance as intermediates in the manufacture of materials of possible</i></p>		

REF ID: A65120

value to the Air Force in diverse applications including antioxidants, lubricity agents, elastomers, flame retardants, and fuel cell catalysts.

The development of methods for the synthesis of organic compounds bearing several  $(R_2N)_2P$  substituents requires the availability of important dialkylaminophosphorus building blocks. In this connection major effects of the size of the dialkylamino group on the resulting dialkylaminophosphorus chemistry were documented for the first time. Thus much of the originally planned chemistry failed when dimethylamino substituents were present owing to the sensitivity of such systems towards strong reducing agents (e.g., lithium and magnesium metals) which frequently led to the conversion of essentially all of the dimethylamino groups to  $(Me_2N)_3P$ . However, much interesting new dialkylaminophosphorus chemistry was developed by using larger dialkylamino groups. Thus the compounds  $(Et_2N)_2PH$  and  $(iPr_2N)_2PH$  were found to be isolable whereas we have been unable to isolate or even detect  $(Me_2N)_2PH$  using analogous methods. Similarly the cyclotetraphosphines  $(iPr_2N)_4P_4$  and  $(Cx_2N)_4P_4$  ( $Cx$  = cyclohexyl) are isolable and  $(Et_2N)_4P_4$  has tentatively been detected whereas we have not yet been able to isolate or even detect the analogous  $(Me_2N)_4P_4$  using similar methods. Other achievements from this research project include the isolation of the first  $(R_2N)(R'O)PH$  derivatives (i.e.,  $R$  = isopropyl,  $R'$  = methyl, ethyl, isopropyl, and tert-butyl), the detection of the first  $R_2NPH_2$  derivatives containing hydrocarbon  $R$  groups (i.e.,  $R$  = cyclohexyl or isopropyl or  $R_2N$  = 2,2,6,6-tetramethylpiperidino), the first preparation of a ditertiary phosphine of the type  $(R_2N)_2PCH_2CH_2P(NR_2)_2$  by the base-catalyzed addition of an  $(R_2N)_2PH$  derivative to  $(R_2N)_2PCH=CH_2$ , and the development of some metal carbonyl chemistry of  $(iPr_2N)_2PH$ .

AFOSR Program Manager: Dr. Anthony M. Matuszko

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## INTRODUCTION

The original scientific objective of this basic research program was the understanding of the synthesis and chemical reactivity of organic compounds consisting of a carbon backbone bearing several bis(dialkylamino)phosphino substituents,  $(R_2N)_2P$ . This class of organophosphorus compounds, which has received very little attention, is of potential importance as intermediates in the manufacture of materials of possible value to the Air Force in diverse applications including antioxidants, lubricity agents, elastomers, flame retardants, and fuel cell catalysts.

The development of methods for the synthesis of organic compounds bearing several  $(R_2N)_2P$  substituents requires information on the preparation and properties of important dialkylaminophosphorus building blocks. In this connection major effects of the size of the dialkylamino group on the resulting dialkylaminophosphorus chemistry were documented for the first time. Thus much of the chemistry outlined in the original proposal<sup>1</sup> using dimethylamino groups as terminal groups failed owing to the sensitivity of such systems towards strong reducing agents (e.g., lithium and magnesium metals) which frequently led to conversion of essentially all of the dimethylamino groups to tris(dimethylamino)phosphine. However, much interesting new dialkylaminophosphorus chemistry was developed by using larger dialkylamino groups such as diethylamino and diisopropylamino. Thus the compounds  $(Et_2N)_2PH$  and  $(iPr_2N)_2PH$  are isolable whereas we have been unable to isolate or even detect  $(Me_2N)_2PH$  using analogous methods. Similarly the cyclotetraphosphines  $(iPr_2N)_4P_4$  and  $(Cx_2N)_4P_4$  ( $Cx$  = cyclohexyl) are isolable and  $(Et_2N)_4P_4$  is detectable whereas we have not yet been able to isolate or even detect the analogous  $(Me_2N)_4P_4$ . Other achievements from this research project include the isolation of the first  $(R_2N)(R'O)PH$  derivatives, the detection of the first  $R_2NPH_2$  derivatives containing hydrocarbon R groups, the first preparation of a ditertiary phosphine of the type  $(R_2N)_2PCH_2CH_2P(NR_2)_2$  by the base-catalyzed addition of an  $(R_2N)_2PH$  derivative to  $(R_2N)_2PCH=CH_2$ , and the development of some metal carbonyl chemistry of  $(iPr_2N)_2PH$ .

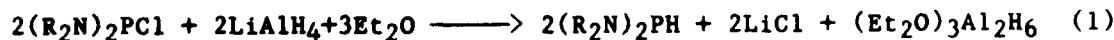
NEW RESULTS FROM THIS RESEARCH PROGRAM

(1) General Comments

Many of the compounds prepared during the course of this research project are too unstable to be purified completely and to be shipped to analytical laboratories. Therefore spectroscopic techniques available within the chemistry department at the University of Georgia were most important for the characterization of such compounds. In this connection mass spectrometry and phosphorus-31 NMR spectroscopy were especially useful. Mass spectrometry allowed determination of the molecular weight and fragmentation patterns (thereby suggesting certain structural features) for new compounds sufficiently stable in the vapor phase including  $(Et_2N)_2PH$  and several of the  $(R_2N)(R'O)PH$  derivatives. Phosphorus-31 NMR spectroscopy was particularly useful for the new phosphorus-hydrogen derivatives (Table 1) since running such spectra both with and without proton decoupling provided direct information regarding the number of hydrogen atoms bonded to each phosphorus atom. This was particularly important in connection with the identification of the  $R_2NPH_2$  derivatives which have so far defied isolation. Some of the cyclotetraphosphines, bis(diisopropylamino)phosphine, the diphosphines  $(R_2N)_2PCH_2CH_2P(NR_2)_2$ , and the metal carbonyl derivatives of  $(iPr_2N)_2PH$  were stable enough that they could be characterized by normal methods including elemental analyses (C, H, and N) on fully purified samples.

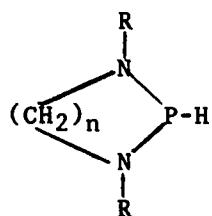
(2) Bis(dialkylamino)phosphines,  $(R_2N)_2PH$

Treatment of bis(dialkylamino)chlorophosphines,  $(R_2N)_2PCl$ , with  $LiAlH_4$  was found to be a useful method for the preparation of the corresponding bis(dialkylamino)phosphines,  $(R_2N)_2PH$ , according to the following reaction:



Using this reaction the diisopropylamino derivative  $(iPr_2N)_2PH$  could readily be isolated in good yield and the diethylamino derivative  $(Et_2N)_2PH$  could be isolated with difficulty in poor yield. However, preparation of  $(Me_2N)_2PH$  by the same method was completely unsuccessful.

Similarly the cyclic derivatives  $(\text{CH}_2)_n(\text{NCMe}_3)_2\text{PH}$  (I:  $\text{R} = (\text{CH}_3)_3\text{C}$ ;  $n = 2$  and  $3$ ) could be prepared but the less sterically hindered



$(\text{CH}_2)_2(\text{NMe})_2\text{PH}$  (I:  $\text{R} = \text{CH}_3$ ,  $n = 2$ ) could not be prepared. The isolable  $(\text{R}_2\text{N})_2\text{PH}$  derivatives are vacuum distillable liquids which are so sensitive towards air oxidation that a tissue impregnated with the liquid burns in the air. Suggestive evidence for the  $(\text{Et}_2\text{O})_3\text{Al}_2\text{H}_6$  by-product is provided by gas chromatography/mass spectrometric analyses of several different  $\text{LiAlH}_4/\text{R}_2\text{NPCl}_2$  and  $\text{LiAlH}_4/(\text{R}_2\text{N})_2\text{PCl}$  reaction mixtures which give a fraction exhibiting the ions  $\text{Al}_2\text{H}_5(\text{OEt}_2)_n^+ (n = 3, 2, \text{ and } 1)$  in the mass spectrum.

The compound  $(\text{CH}_2)_3(\text{NCMe}_3)_2\text{PH}$  (I:  $\text{R} = (\text{CH}_3)_3\text{C}$ ;  $n = 3$ ) has been previously prepared by the reduction of the corresponding chlorophosphine  $(\text{CH}_2)_3(\text{NCMe}_3)_2\text{PCl}$  with tri-n-butyltin hydride.<sup>2</sup> However, the analogous reaction of  $(\text{iPr}_2\text{N})_2\text{PCl}$  with  $(\text{n-C}_4\text{H}_9)_3\text{SnH}$  in our hands gives only  $\text{iPr}_2\text{NH}$ ,  $(\text{n-C}_4\text{H}_9)_3\text{SnCl}$ , and ill-defined yellow insoluble phosphorus products with no evidence for the formation of any  $(\text{iPr}_2\text{N})_2\text{PH}$ .

### (3) Chemical Reactivity of Bis(dialkylamino)phosphines

The bis(dialkylamino)phosphines, particularly the readily preparable and isolable  $(\text{iPr}_2\text{N})_2\text{PH}$ , have proven to be useful intermediates for the preparation of other interesting bis(dialkylamino)phosphorus derivatives. Our more interesting results to date include the following:

(a) Alcoholytic reactions: The diisopropylamino groups in  $(\text{iPr}_2\text{N})_2\text{PH}$  undergo successive alcoholytic reactions with the alcohols  $\text{ROH}$  ( $\text{R} = \text{methyl, ethyl, isopropyl, and tert-butyl}$ ) to form  $(\text{iPr}_2\text{N})(\text{RO})\text{PH}$  and  $(\text{RO})_2\text{PH}$  which are identified by their phosphorus-31 NMR spectra (Table 1). The derivatives  $(\text{iPr}_2\text{N})(\text{RO})\text{PH}$  ( $\text{R} = \text{methyl, ethyl, isopropyl, and tert-butyl}$ ) can be isolated by vacuum distillation as air-sensitive liquids but

TABLE 1  
NEW PHOSPHORUS-HYDROGEN COMPOUNDS PREPARED  
DURING THE COURSE OF THIS RESEARCH PROJECT <sup>a</sup>

Compound	Phosphorus-31 NMR <sup>b</sup>		Other Characterization <sup>c</sup>
	$\delta$ (P)	$^1J(P-H)$ , Hz.	
(iPr <sub>2</sub> N) <sub>2</sub> PH	42.1d	254	anal., mass spec., $\nu(PH)=2225$
(Et <sub>2</sub> N) <sub>2</sub> PH	77.0d	249	mass spec., $\nu(PH)=2272$
(CH <sub>2</sub> ) <sub>3</sub> (NCMe <sub>3</sub> ) <sub>2</sub> PH	49.7d	216	mass spec., known compound <sup>d</sup>
(CH <sub>2</sub> ) <sub>2</sub> (NCMe <sub>3</sub> ) <sub>2</sub> PH	57.9d	156	mass spec., $\nu(PH)=2340$
(iPr <sub>2</sub> N)(MeO)PH	106.5d	244	mass spec., $\nu(PH)=2280$
(iPr <sub>2</sub> N)(EtO)PH	100.9d	242	mass spec., $\nu(PH)=2280$
(iPr <sub>2</sub> N)(iPrO)PH	95.4d	249	mass spec., $\nu(PH)=2350$
(iPr <sub>2</sub> N)(tBuO)PH	81.0d	242	mass spec., $\nu(PH)=2280$
(Et <sub>2</sub> N)(EtO)PH	121.6d	234	
(Et <sub>2</sub> N)(tBuO)PH	106.7d	254	
(MeO) <sub>2</sub> PH	172.0d	195	
(EtO) <sub>2</sub> PH	161.1d	197	
(iPrO) <sub>2</sub> PH	151.2d	201	
(tBuO) <sub>2</sub> PH	115.0d	205	
(CH <sub>2</sub> ) <sub>3</sub> (CMe <sub>2</sub> ) <sub>2</sub> NPH <sub>2</sub>	-86.6t	200	$\nu(PH)=2280, 2210$
(cC <sub>6</sub> H <sub>11</sub> ) <sub>2</sub> NPH <sub>2</sub>	-72.3t	198	$\nu(PH)=\sim 2200$ (broad)
iPr <sub>2</sub> NPH <sub>2</sub>	-82.9t	196	
[(iPr <sub>2</sub> N) <sub>2</sub> PH]Fe(CO) <sub>4</sub>	93.9d	410	anal., $\nu(CO)$
[(iPr <sub>2</sub> N) <sub>2</sub> PH]Cr(CO) <sub>5</sub>	91.8d	363	anal., $\nu(CO)$
[(iPr <sub>2</sub> N) <sub>2</sub> PH]Mo(CO) <sub>5</sub>	67.0d	356	anal., $\nu(CO)$
[(iPr <sub>2</sub> N) <sub>2</sub> PH]W(CO) <sub>5</sub>	41.7d	359	anal., $\nu(CO)$
[(iPr <sub>2</sub> N) <sub>2</sub> PH]Mn(CO) <sub>2</sub> (C <sub>5</sub> H <sub>5</sub> ) 123.1d	381		$\nu(CO)$

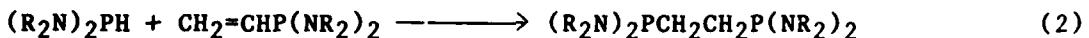
(a) The phosphorus-31 NMR data listed in this table were obtained from compounds prepared as follows (see text): (R<sub>2</sub>N)<sub>2</sub>PH and R<sub>2</sub>NPH<sub>2</sub>: LiAlH<sub>4</sub> reduction of the corresponding (R<sub>2</sub>N)<sub>2</sub>PCl or R<sub>2</sub>NPCl<sub>2</sub> derivative; (R<sub>2</sub>N)(R'O)PH and (R'O)<sub>2</sub>PH: alcoholysis of the corresponding (R<sub>2</sub>N)<sub>2</sub>PH derivative; (iPr<sub>2</sub>N)<sub>2</sub>PH metal carbonyl derivatives: reaction of (iPr<sub>2</sub>N)<sub>2</sub>PH with an appropriate metal carbonyl complex generally involving displacement of a coordinated tetrahydrofuran ligand.

(b) The phosphorus-31 NMR spectra were all run with and without proton decoupling. Multiplicities (d = doublet, t = triplet) represent the major splittings (i.e.,  $^1J(P-H)$ ) obtained from spectra without proton decoupling.

(c) The other methods for characterization of these compounds are as follows: anal.: correct analyses for carbon, hydrogen, and nitrogen; mass spec.: reasonable mass spectrum including observation of the expected molecular ion;  $\nu(PH)$ : observation of the expected infrared phosphorus-hydrogen stretching frequencies at the indicated positions in the 2200-2350 cm.<sup>-1</sup> region;  $\nu(CO)$ : a pattern of metal carbonyl  $\nu(CO)$  stretching frequencies in the 2100-1800 cm.<sup>-1</sup> region similar to that of analogous metal carbonyl complexes of other phosphines.

the derivatives  $(RO)_2PH$  generally decompose upon attempted vacuum distillation. Similar alcoholysis reactions of  $(Et_2N)_2PH$  give the less stable  $(Et_2N)(EtO)PH$  and  $(Et_2N)(Me_3CO)PH$ , which are detectable in solution by their phosphorus-31 NMR spectra (Table 1).

(b) Base-catalyzed addition reactions: Addition of  $(R_2N)_2PH$  to the vinyl double bond in  $(R_2N)_2PCH=CH_2$  catalyzed by potassium hydride gives in some cases the corresponding diphosphine  $(R_2N)_2PCH_2CH_2P(NR_2)_2$  according to the following reaction:



The success of this reaction depends upon the size of the  $R_2N$  group. Thus this reaction succeeds for  $R_2N = Et_2N$  or  $(CH_2)_3(NCMe_3)_2$  but fails for the larger  $iPr_2N$  group.

(c) Metal carbonyl chemistry: Preliminary experiments indicate that  $(iPr_2N)_2PH$  forms a variety of rather stable metal carbonyl complexes (Table 1). Thus the group VI metal carbonyl derivatives  $[(iPr_2N)_2PH]M(CO)_5$  ( $M = Cr, Mo, and W$ ) can be prepared by displacement of coordinated tetrahydrofuran (THF) from the corresponding  $(THF)M(CO)_5$  derivative. A similar preparative method works for the cyclopentadienylmanganese derivative  $[(iPr_2N)_2PH]Mn(CO)_2C_5H_5$ . The iron compound  $[(iPr_2N)_2PH]Fe(CO)_4$  was obtained from the reaction of  $Fe_2(CO)_9$  with  $(iPr_2N)_2PH$ . These metal carbonyl complexes of  $(iPr_2N)_2PH$  are solids which can be readily purified by vacuum sublimation. They are considerably more air-stable than the free ligand. Thus the solid complexes  $[(iPr_2N)_2PH]M(CO)_5$  ( $M = Cr and W$ ) have been exposed to air for several days without noticeable decomposition.

#### (4) Dialkylaminophosphines, $R_2NPH_2$

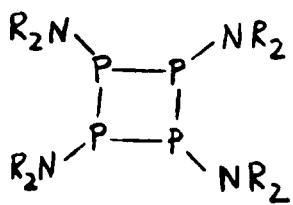
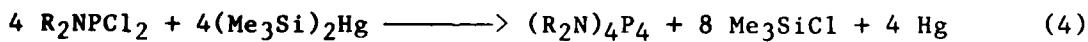
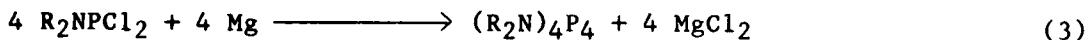
The success noted above in the preparation of  $(R_2N)_2PH$  derivatives from  $LiAlH_4$  and the corresponding  $(R_2N)_2PCl$  derivatives suggested an analogous preparation of  $R_2NPH_2$  derivatives from  $LiAlH_4$  and the corresponding  $R_2NPCl_2$  derivatives. Studies on this reaction have led to the following observations:

(a) The  $R_2NPH_2$  derivatives are less stable than the corresponding  $(R_2N)_2PH$  derivatives and require a larger  $R_2N$  group to be obtainable since only one  $R_2N$  group is available to protect the phosphorus atom from reactions leading to decomposition.

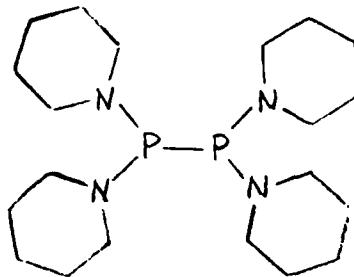
(b) Excess LiAlH<sub>4</sub> must be avoided in its reaction with the R<sub>2</sub>NPCl<sub>2</sub> derivative since excess LiAlH<sub>4</sub> appears to destroy the R<sub>2</sub>NPH<sub>2</sub> derivative possibly through formation of an aluminum hydride complex (see below). Use of the more basic tetrahydrofuran rather than diethyl ether as the solvent for the reaction with LiAlH<sub>4</sub> seems to reduce the tendency for aluminum hydride byproducts to complex with the desired R<sub>2</sub>NPH<sub>2</sub> product. To date, we have obtained phosphorus-31 NMR evidence (Table 1) for the formation of the three R<sub>2</sub>NPH<sub>2</sub> derivatives (R<sub>2</sub>N = 2,2,6,6-tetramethylpiperidinyl, dicyclohexylamino, and diisopropylamino) from reactions of the corresponding R<sub>2</sub>NPCl<sub>2</sub> derivative with LiAlH<sub>4</sub> in tetrahydrofuran using a 1:1 R<sub>2</sub>NPCl<sub>2</sub>/LiAlH<sub>4</sub> molar ratio. Attempts to isolate any of these products by distillation led to decomposition giving non-volatile brown solids. The effect of excess LiAlH<sub>4</sub> on this reaction is illustrated by a reaction of 2,2,6,6-(CH<sub>2</sub>)<sub>3</sub>(CMe<sub>2</sub>)<sub>2</sub>NPCl<sub>2</sub> with LiAlH<sub>4</sub> in a 1:2 R<sub>2</sub>NPCl<sub>2</sub>/LiAlH<sub>4</sub> molar ratio where phosphorus-31 NMR of the reaction mixture indicates a resonance at  $\delta$ +189.5 (triplet, J(P-H) = 200 Hz.) which on the basis of its low field position is formulated as an aluminum hydride complex of 2,2,6,6-(CH<sub>2</sub>)<sub>3</sub>(CMe<sub>2</sub>)<sub>2</sub>NPH<sub>2</sub>. We have not been able to isolate this product in sufficient quantity for more detailed characterization.

(5) Tetrakis(dialkylamino)cyclotetraphosphines, (R<sub>2</sub>N)<sub>4</sub>P<sub>4</sub>

Tetrakis(dialkylamino)cyclotetraphosphines, (R<sub>2</sub>N)<sub>4</sub>P<sub>4</sub> (II) can be obtained in some cases by the reductive dechlorination of the corresponding R<sub>2</sub>NPCl<sub>2</sub> derivatives. In our hands the two most useful reagents for this reductive dechlorination are the heterogeneous magnesium metal (equation 3) and the homogeneous (Me<sub>3</sub>Si)<sub>2</sub>Hg (equation 4).



II



III

The former method is more convenient and less expensive when it works and has been used to prepare the cyclotetraphosphines  $(iPr_2N)_4P_4$  (II: R = isopropyl) and  $(Cx_2N)_4P_4$  (II: R = cyclohexyl) which have been characterized by elemental analyses (C, H, N), osmometric molecular weight determinations in benzene, and mass spectra as well as phosphorus-31 resonances at  $\delta$ 18.7 (R = isopropyl) and  $\delta$ 25.1 (R = cyclohexyl). In addition, reactions of the piperidino derivatives  $2,6-(CH_2)_3(CHMe)_2NPCl_2$  and  $2,2,6,6-(CH_2)_3(CMe_2)_2NPCl_2$  with magnesium give white solids suggested by their phosphorus-31 NMR chemical shifts of  $\delta$ +50.2 and  $\delta$ +50.5 to be similar  $(R_2NP)_n$  cyclopolyphosphines but these products have not yet been isolated in the pure state. Reactions of the less sterically hindered  $Et_2NPCl_2$  and  $Me_2NPCl_2$  with magnesium gives 70-75% yields of the corresponding  $(R_2N)_3P$  derivative with no evidence for the formation of any of the corresponding cyclotetraphosphine  $(R_2N)_4P_4$ . Reaction of the piperidino derivative  $(CH_2)_5NPCl_2$  with magnesium does not give any evidence for the formation of a cyclopolyphosphine  $[(CH_2)_5NP]_n$  but instead gives the biphosphine  $[(CH_2)_5N]_2P-P[N(CH_2)_5]_2$  (III) in 66% yield based on available piperidino groups.

The silylmercury reagent,  $(Me_3Si)_2Hg$ , is soluble in organic solvents such as pentane and benzene and therefore is a homogeneous rather than a heterogeneous dechlorinating reagent. This allows reactions to be run under milder conditions. Furthermore such reactions can be followed using phosphorus-31 NMR spectroscopy. This silylmercury reagent can be used not only to prepare (in 35% isolated yield) the diisopropylamino derivative  $(iPr_2N)_4P_4$  (II: R = isopropyl) but also to generate at least in solution the diethylamino derivative  $(Et_2N)_4P_4$  and the piperidino derivative  $[(CH_2)_5NP]_n$  as indicated by phosphorus-31 NMR resonances at  $\delta$ 45.5 and  $\delta$ 40.8, respectively, for the major components of the  $R_2NPCl_2/(Me_3Si)_2Hg$  reaction mixture. We are currently trying to isolate these new cyclopolyphosphines in the pure state.

Our most detailed studies on tetrakis(dialkylamino)cyclotetraphosphines have been done on the diisopropylamino derivative  $(iPr_2N)_4P_4$  (II: R = isopropyl) which can be obtained in 50-60% yield as a white sublimable solid, m.p. 197-198°C, by the reaction of  $iPr_2NPCl_2$  with magnesium in boiling tetrahydrofuran followed by hydrolysis with aqueous tetrasodium ethylenediamine tetraacetate. We have prepared more than

50 g. of this cyclotetraphosphine by this method and have submitted a sample to Dr. C. Tamborski of the Air Force Materials Laboratory for thermal stability testing by thermogravimetric analyses. We have also made the following observations on the chemical reactivity of  $(iPr_2N)_4P_4$  (II: R =  $Me_2CH$ ):

(a) Air: The steric hindrance of the eight isopropyl groups in  $(iPr_2N)_4P_4$  makes this compound stable towards air oxidation.

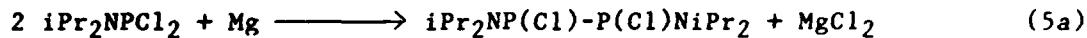
(b) Halogen reagents: Phosphorus-31 NMR of reaction mixtures indicate that halogens and hydrogen halides readily react with  $(iPr_2N)_4P_4$  with cleavage of the  $P_4$  ring to give  $iPr_2NPX_2$  as the major product.

(c) Sulfur: Sulfur reacts with  $(iPr_2N)_4P_4$  in boiling benzene to give a white solid, m.p. 118-120°C, suggested by analytical data (C, H, N) to be  $iPr_2NP(S)-S-S-P(S)NiPr_2$ . A similar product has been obtained by reaction of tetra-*t*-butylcyclotetraphosphine with sulfur.<sup>3</sup> Boiling  $(iPr_2N)_4P_4$  in carbon disulfide for 24 hr. led to no change.

(d) Photolysis: Photolysis of  $(iPr_2N)_4P_4$  is of interest because of the possibility of generating interesting phosphinidene intermediates which might have unusual chemistry because of the relatively large size of the diisopropylamino groups. Ultraviolet irradiation of  $(iPr_2N)_4P_4$  in diethyl ether solution was found to give a yellow precipitate which did not have the stoichiometry  $(iPr_2NP)_n$  expected for a polymer generated from a diphosphene or phosphinidene. In an attempt to trap any diphosphene or phosphinidene intermediates as a more stable adduct, the ultraviolet irradiation was repeated in the presence of 2,3-dimethylbutadiene. However, the same yellow precipitate was obtained.

(e) Metals and metal complexes: The steric hindrance of the diisopropylamino groups in  $(iPr_2N)_4P_4$  makes the  $P_4$  ring relatively unreactive towards reactions with alkali metals and with metal carbonyls. Some evidence has been obtained for limited chemical reactivity towards potassium metal in boiling tetrahydrofuran or dioxane and towards several metal carbonyl derivatives including  $Mo(CO)_6$  in boiling methylcyclohexane and  $Fe_2(CO)_9$  in diethyl ether. However, results are still inconclusive.

During the course of our studies on the preparation of  $(iPr_2N)_4P_4$  by the dechlorination of  $iPr_2NPCl_2$  with magnesium, we have obtained evidence that this reaction proceeds in the following two stages:



The dichlorobiphosphine formed in the first step (equation 5a) is a white solid, m.p. 90-92°C,  $^{31}\text{P}$  NMR: 127.7, which is sensitive to air and water and which can be isolated in 20% yield if the  $\text{iPr}_2\text{NPCl}_2/\text{Mg}$  ratio is 2:1 and if hydrolysis is avoided prior to product isolation. Limited studies suggest that  $\text{iPr}_2\text{NP}(\text{Cl})-\text{P}(\text{Cl})\text{NiPr}_2$  undergoes cleavage of its phosphorus-phosphorus bond under relatively mild conditions (e.g., amines or  $\text{Fe}_2(\text{CO})_9$  at room temperature or below) to give  $\text{iPr}_2\text{NPCl}_2 + (\text{iPr}_2\text{N})_2\text{PCl}$  and/or products derived therefrom.

We have also begun some electrochemical studies on tetrakis(dialkylamino)cyclotetraphosphines,  $(\text{R}_2\text{N})_4\text{P}_4$ , in attempts to prepare the radical cations  $(\text{R}_2\text{N})_4\text{P}_4^+$  or other oxidation products of interest. Cyclic voltammetry of the  $(\text{R}_2\text{N})_4\text{P}_4$  derivatives in 1,2-dimethoxyethane using  $[\text{nBu}_4\text{N}][\text{PF}_6]$  as the supporting electrolyte indicate reversible oxidation waves at  $E_{1/2} = +0.35$  V for  $\text{R} = \text{isopropyl}$  and  $E_{1/2} = +0.275$  V for  $\text{R} = \text{cyclohexyl}$  versus  $\text{Ag}/\text{AgCl}$ . Coulometry on the oxidation of  $(\text{iPr}_2\text{N})_4\text{P}_4$  at an applied potential of +0.5 V suggests that this is a one-electron process as would be the case if the  $(\text{iPr}_2\text{N})_4\text{P}_4^+$  radical cation is formed. Further electrochemical studies on these systems are needed before definite conclusions can be drawn.

#### (6) Tetrakis(dialkylamino)diphosphines, $(\text{R}_2\text{N})_4\text{P}_2$

In 1961<sup>4</sup> the preparation of the diphosphine,  $(\text{Me}_2\text{N})_4\text{P}_2$ , was reported using the reaction of  $(\text{Me}_2\text{N})_2\text{PCl}$  with sodium metal in a hydrocarbon solvent. From time to time throughout the course of this project we tried to repeat this reaction or to prepare  $(\text{Me}_2\text{N})_4\text{P}_2$  by the reaction of  $(\text{Me}_2\text{N})_2\text{PCl}$  with lithium or magnesium metal in tetrahydrofuran solution. In our hands such reactions yielded little or none of the desired  $(\text{Me}_2\text{N})_4\text{P}_2$  with the major product being  $(\text{Me}_2\text{N})_3\text{P}$ .

In view of these difficulties in preparing  $(\text{Me}_2\text{N})_4\text{P}_2$  for some of the proposed chemistry discussed in detail in the original proposal, we were particularly interested to find that the reaction of the mono-piperidino derivative  $(\text{CH}_2)_5\text{NPCl}_2$  with magnesium metal in tetrahydrofuran gave the biphosphine  $[(\text{CH}_2)_5\text{N}]_2\text{P}-\text{P}[\text{N}(\text{CH}_2)_5]_2$  (III) with redistribution of the piperidino groups. The biphosphine III was subsequently prepared

in 70% yield by the more efficient reaction of  $[(\text{CH}_2)_5\text{N}]_2\text{PCl}$  with magnesium metal in boiling tetrahydrofuran.

The availability of III in relatively large quantities as a result of this discovery has prompted a preliminary study of some of its reactions with metal carbonyls. This work, however, was rather disappointing since such reactions led to trivial tris(piperidino)phosphine metal carbonyl complexes through further redistribution of the piperidino groups in  $[(\text{CH}_2)_5\text{N}]_2\text{P-P}[\text{N}(\text{CH}_2)_5]_2$  (III) upon reaction with metal carbonyls. New but uninteresting tris(piperidino)phosphine metal carbonyl derivatives isolated in the pure state from reactions of III with metal carbonyls include  $[(\text{CH}_2)_5\text{N}]_3\text{PM}(\text{CO})_5$  (M = Cr and Mo) from reactions with  $\text{M}(\text{CO})_6$ ,  $\{[(\text{CH}_2)_5\text{N}]_3\text{P}\}_2\text{Fe}(\text{CO})_3$  from a reaction with  $\text{Fe}_2(\text{CO})_9$ , and the ionic  $[\text{trans-}\{[(\text{CH}_2)_5\text{N}]_3\text{P}\}_2\text{Co}(\text{CO})_3]^+[\text{Co}(\text{CO})_4]^-$  from a reaction with  $\text{Co}_2(\text{CO})_8$ . These compounds have been characterized by correct C, H, and N analyses and infrared spectra in the  $2100$ - $1800\text{ cm.}^{-1}$   $\nu(\text{CO})$  region corresponding to those reported<sup>5</sup> for analogous complexes of tris(dimethylamino)phosphine.

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PUBLICATIONS AND MEETING PRESENTATIONS SUPPORTED BY  
AIR FORCE GRANT AFOSR-81-0051

(A) Published and in press

- (1) King, R. B.; Sadanani, N. D.; Sundaram, P. M. "Novel Diisopropylamino Derivatives of Trivalent Phosphorus," Chem. Comm. 1983, 477.
- (2) King, R. B.; Sadanani, N. D.; Sundaram, P. M. "New Dialkylamino Derivatives of Trivalent Phosphorus," Phosphorus and Sulfur in press.
- (3) King, R. B.; Sundaram, P. M. "Bis(dialkylamino)phosphines," J. Org. Chem., submitted for publication.

(B) Publication anticipated after completion of experiments currently in progress

- (4) King, R. B.; Sadanani, N. D. "Cyclopolyphosphines Having Dialkylamino Terminal Groups."
- (5) King, R. B.; Sadanani, N. D. "Dialkylaminophosphines."
- (6) King, R. B.; Fu, W.-K. "Metal Carbonyl Chemistry of Bis(diisopropylamino)phosphine."

(C) Meeting presentations

- (7) King, R. B.; Sadanani, N. D.; Sundaram, P. M. "Diisopropylaminophosphorus Chemistry," paper presented by R. B. King at the 185th National Meeting of the American Chemical Society, Seattle, Washington, March, 1983: paper INOR 34 in abstracts.
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